Supporting Information

# "Synthesis of macrocyclic receptors with intrinsic fluorescence featuring quinizarin moities"

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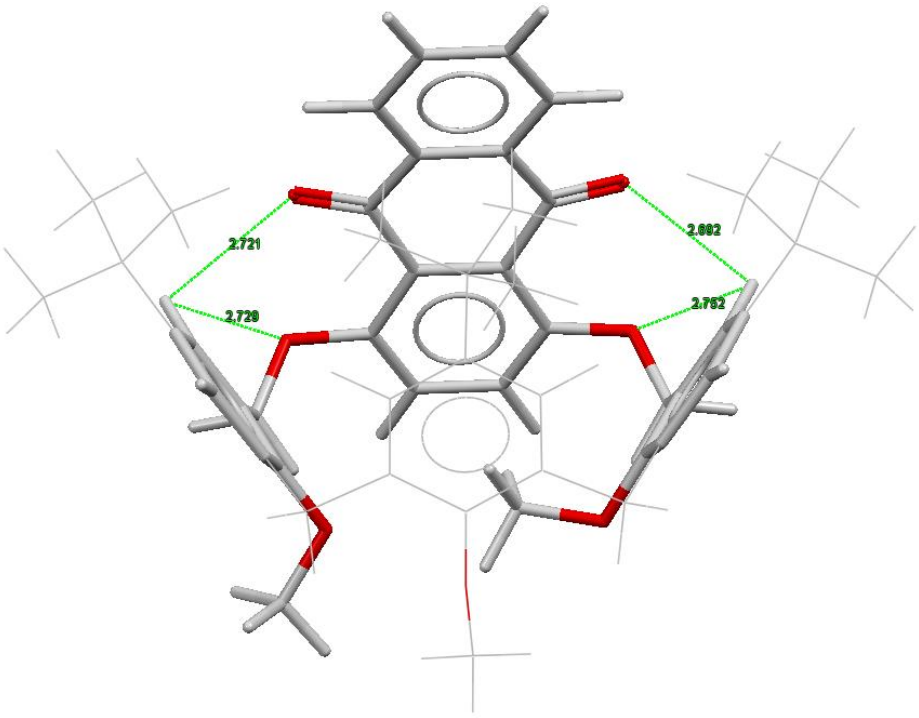
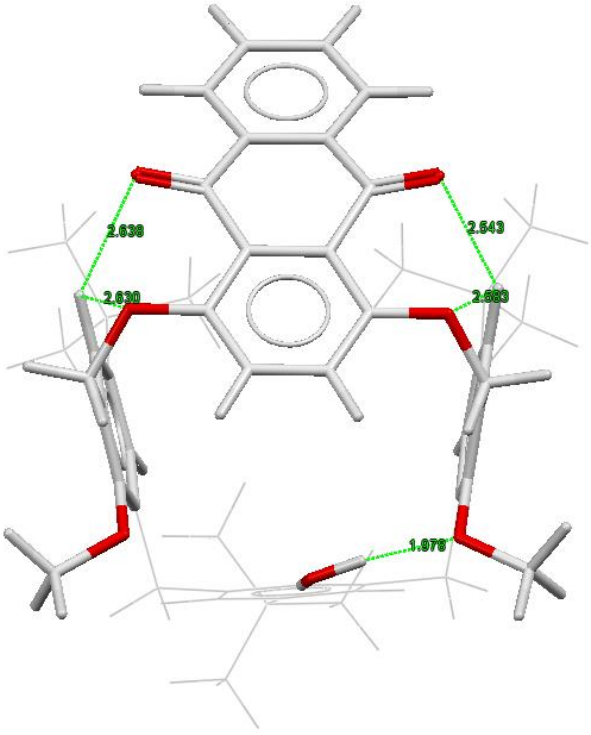
## 1. Energy-minimization




a)




b)

**Figure S1.** Energy-minimized structures of **1** (a) and **2** (b). (MacroModel V.9.8, OPLS_2001 forcefield, MCMM, 1,000 steps.)

## 2. X-ray crystallography

Compound **4**

Crystallization of **4** from ethyl acetate yielded colorless crystals in the monoclinic space group $P2_1/n$. The asymmetric unit contains one molecule; none of the solvent is included in the crystal lattice. The aromatic ring A is turned away from the other two anisole moieties delivering a highly twisted molecule (Fig. S2) as methylation of the phenolic hydroxyl groups destroys the hydrogen bonding pattern found in **3**.[1] As stabilizing for the molecular structure we found weak C-H···O-contacts [d(O···H) = 2.39 - 2.48 Å] involving the two methylene bridges and two of the methoxy oxygens O1 and O2. The crystal packing is realized by a combination of weak C-H···O- and C-H···π-interactions (Table S1, Fig. S3).

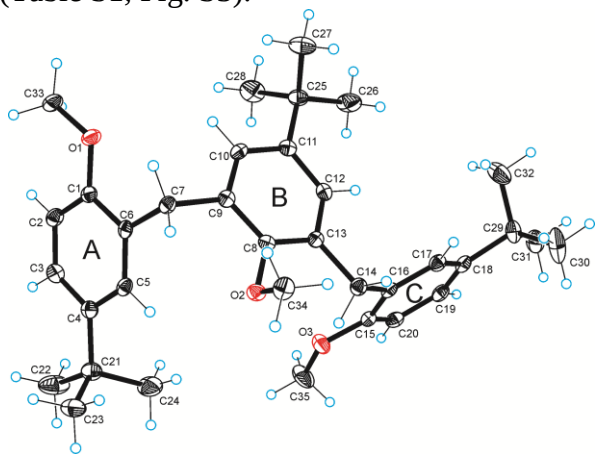



**Figure S2.** Molecular structure of **4**.

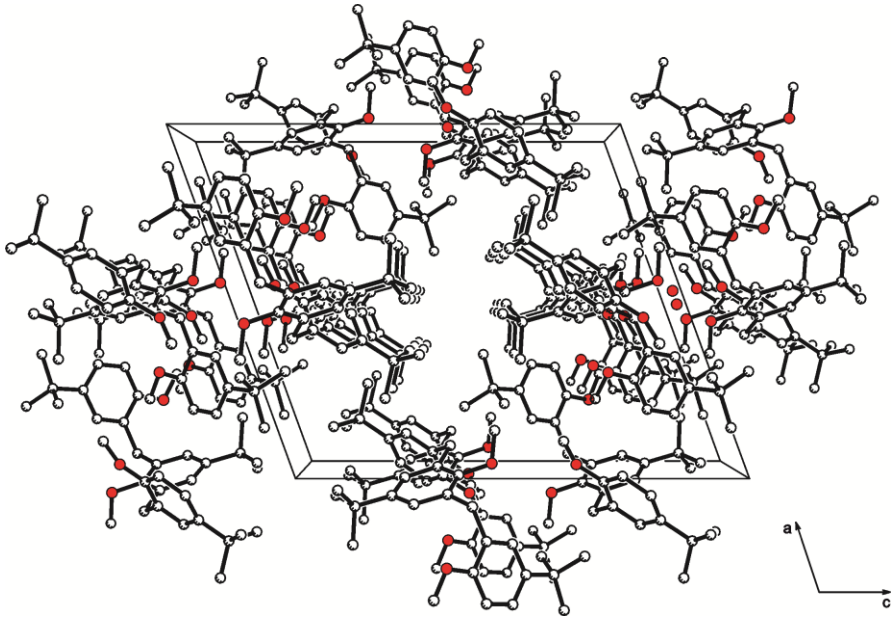



**Figure S3.** Packing diagram of **4** viewed down the crystallographic *b* axis. H atoms are omitted for clarity.

[1] Thuéry, P.; Asfari, Z.; Nierlich, M.; Vicens, J.; Masci, B. *Polyhedron* **2002**, *21*, 1949-1956.

**Table S1. Crystal data and selected details of the data collection and refinement calculations of compounds 1, 2 and 4.**

| | **1** | **2** | **4** |
|---|---|---|---|
| empirical formula | 2 $C_{50}H_{54}O_7$ · 2 $CH_3CN$ · $CHCl_3$ | $C_{50}H_{54}O_7$ · 3 $CH_3CN$ | $C_{35}H_{48}O_3$ |
| formula weight | 1735.40 | 890.12 | 516.73 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | *C*2/*c* | $P2_1/n$ | $P2_1/c$ |
| *a*/Å | 32.740(5) | 14.6715(5) | 15.5715(3) |
| *b*/Å | 14.888(2) | 21.2801(7) | 11.2487(2) |
| *c*/Å | 38.686(5) | 15.6545(5) | 18.7684(4) |
| $\alpha$/° | 90.00 | 90.00 | 90.00 |
| $\beta$/° | 99.017(11) | 97.2810(10) | 110.0590(10) |
| $\gamma$/° | 90.00 | 90.00 | 90.00 |
| *V*/Å$^3$ | 18624(5) | 4848.1(3) | 3088.04(10) |
| *Z* | 8 | 4 | 4 |
| *F*(000) | 7504 | 1904 | 1128 |
| $D_c$/g cm$^{-3}$ | 1.258 | 1.219 | 1.111 |
| $\mu$/mm$^{-1}$) | 0.165 | 0.080 | 0.069 |
| data collection: | | | |
| temperature/K | 100(2) | 100(2) | 100(2) |
| no. of collected reflections | 262554 | 132312 | 23361 |
| within the $\theta$-limit/° | 1.90-25.00 | 1.70-25.00 | 2.77-25.00 |
| index ranges ±*h*, ±*k*, ±*l* | -38/38, -17/17, -46/45 | -17/17, -2125, -18/18 | -18/18, -13/10, -22/21 |
| no. of unique reflections | 16388 | 8529 | 5429 |
| $R_{int}$ | 0.0360 | 0.0340 | 0.0399 |
| weighting expression *w*[a] | $[\sigma^2(F_o^2)+(0.0337P)^2+43.8450P]^{-1}$ | $[\sigma^2(F_o^2)+(0.0426P)^2+1.9870P]^{-1}$ | $[\sigma2(F_o^2)+(0.0490P)^2+0.5143P]^{-1}$ |
| no. refined parameters | 1205 | 610 | 355 |
| no. reflns used [$I>2\sigma(I)$] | 14686 | 7378 | 4192 |
| $R_1$, $wR_2$ [$l>2\sigma(l)$] | 0.0497, 0.0438 | 0.0352, 0.0882 | 0.0386, 0.0901 |
| $R_1$, $wR_2$ (all data) | 0.1027, 0.1000 | 0.0431, 0.0920 | 0.0573, 0.0969 |
| *S* (=Goodness of fit on $F^2$) | 1.033 | 1.056 | 1.032 |
| final $\Delta\rho_{max}/\Delta\rho_{min}$ /e Å$^{-3}$ | 1.203/-1.062 | 0.263/-0.261 | 0.179/-0.195 |

[a] $P = (F_o^2 + 2F_c^2)/3$.

**Table S2. Distances and angles of hydrogen bonding interactions of 1, 2 and 4**

| atoms | symmetry | distances (Å) | | angle (°) |
|---|---|---|---|---|
| | | D···A | H···A | D–H···A |
| **1** | | | | |
| C33-H33B···O6 | 1-*x*, *y*, 0.5-*z* | 3.198(3) | 2.46 | 132 |
| C37-H37···O3 | *x*, *y*, *z* | 3.354(2) | 2.43 | 166 |
| C38-H38···O1 | *x*, *y*, *z* | 3.325(2) | 2.40 | 164 |
| C82-H82B···O7 | *x*, *y*, *z* | 3.478(2) | 2.67 | 148 |
| C85-H85A···O13 | 1-*x*, 1-*y*, -*z* | 3.359(2) | 2.46 | 151 |
| C87-H87···O10 | *x*, *y*, *z* | 3.571(2) | 2.64 | 166 |
| C88-H88···O8 | *x*, *y*, *z* | 3.265(2) | 2.32 | 173 |
| C100-H10B···O14 | 1-*x*, 1-*y*, -*z* | 3.496(2) | 2.53 | 166 |
| C1I-H1I···O12 | *x*, *y*, 1+*z* | 3.436(2) | 2.58 | 143 |
| C1I-H1I···O13 | *x*, *y*, 1+*z* | 3.049(2) | 2.14 | 151 |
| C1G-H1G2···O2 | *x*, *y*, *z* | 3.537(2) | 2.57 | 170 |
| C1H-H1H2···O9 | 0.5+*x*, -0.5+*y*, *z* | 3.523(2 | 2.56 | 169 |
| C26-H26A···centroid C | 1.5-*x*, -0.5+*y*, 0.5-*z* | 3.642(3) | 2.70 | 160 |
| C27-H27A···centroid A | 1.5-*x*, 0.5+*y*, 0.5-*z* | 3.622(2) | 2.75 | 148 |
| C1G-H1G3···centroid A | *x*, *y*, *z* | 3.649(2 | 2.90 | 134 |
| C1H-H1H3···centroid A‘ | 0.5+*x*, -0.5+*y*, *z* | 3.636(2) | 2.88 | 135 |
| C1I-Cl1I···centroid B‘ | *x*, -1+*y*, 1+*z* | 3.505(1) | | 159 |
| **2** | | | | |
| O2-H2···O3 | *x*, *y*, *z* | 2.921(1) | 2.11 | 162 |
| C7-H7B···O1 | *x*, *y*, *z* | 2.886(2) | 2.41 | 109 |
| C7-H7B···O2 | *x*, *y*, *z* | 2.826(2) | 2.46 | 101 |
| C12-H12···O6 | -0.5+*x*, 0.5-*y*, 0.5+*z* | 3.597(2) | 2.66 | 169 |
| C14-H14B···O3 | *x*, *y*, *z* | 2.870(2) | 2.44 | 105 |
| C27-H27A···O5 | -0.5+*x*, 0.5-*y*, 0.5+*z* | 3.598(2) | 2.66 | 161 |
| C33-H33C···N1I | *x*, *y*, *z* | 3.221((2) | 2.61 | 120 |
| C34-H34B···N1H | *x*, *y*, *z* | 3.397(2) | 2.55 | 145 |
| C35-H35B···O3 | *x*, *y*, *z* | 2.890(2) | 2.44 | 107 |
| C37-H37···O3 | *x*, *y*, *z* | 3.591(2) | 2.75 | 148 |
| C38-H38···O1 | *x*, *y*, *z* | 3.328(2) | 2.49 | 148 |
| C50-H50B···O1 | *x*, *y*, *z* | 2.848(2) | 2.38 | 108 |
| C2G-H2G3···O7 | 1-*x*, -*y*, -*z* | 3.184(2) | 2.33 | 146 |
| C2H-H2H1···O1 | *x*, *y*, *z* | 3.357(2) | 2.65 | 129 |
| C2H-H2H1···O2 | *x*, *y*, *z* | 3.275(2) | 2.44 | 143 |
| C2H-H2H2···N1G | *x*, *y*, *z* | 3.498(2) | 2.56 | 160 |
| C30-H30C···centroid[a] ACN | -0.5+*x*, 0.5-*y*, -0.5+*z* | 3.729(2) | 2.83 | 153 |
| C32-H32B···centroid B | -0.5+*x*, 0.5-*y*, -0.5+*z* | 3.722(2) | 2.90 | 142 |
| C35-H35A···centroid F | 1-*x*,-*y*,-*z* | 3.587(1) | 2.93 | 124 |
| C2I-H2I1···centroid C | 0.5+*x*, 0.5-*y*, 0.5+*z* | 3.497(1) | 2.61 | 150 |
| C2I-H2I2···centroid A | 0.5+*x*, 0.5-*y*, 0.5+*z* | 3.642(2) | 2.74 | 154 |
| C2I-H2I3···centroid B | 0.5+*x*, 0.5-*y*, 0.5+*z* | 3.500(2) | 2.86 | 124 |
| **4** | | | | |
| C7-H7A···O1 | *x*, *y*, *z* | 2.798(2) | 2.39 | 104 |
| C7-H7B···O2 | *x*, *y*, *z* | 2.849(2) | 2.47 | 102 |
| C14-H14B···O2 | *x*, *y*, *z* | 2.841(2) | 2.48 | 101 |
| C20-H20···O1 | *x*, -1+*y*, *z* | 3.626(2) | 2.68 | 175 |
| C23-H23C···centroid C | 1-*x*, 1-*y*, -*z* | 3.629(2) | 2.91 | 131 |
| C31-H31B···centroid DB2[b] | 0.5-*x*, -0.5+*y*, 0.5-*z* | 3.548(2) | 2.77 | 137 |
| C33-H33B···centroid A | 1.5-*x*, 0.5+*y*, 0.5-*z* | 3.720(1) | 2.82 | 153 |
| C33-H33C···centroid B | 1.5-*x*, 0.5+*y*, 0.5-*z* | 3.612(1) | 2.94 | 126 |
| C34-H34B···centroid DB1[b] | 1-*x*, 2-*y*, -*z* | 3.568(1) | 2.81 | 135 |

[a] Centroid means the centre of gravity of the respective aromatic ring or bonding system. Centroid ACN describes the centroid of the enclosed acetonitrile molecule C2I-C1I-N1I. [b] Centroid DB1 and DB2 mean the centres of the double bonds between C1-C6 and C12-C13, respectively.

## 3. NMR spectra of 1, 2, 4, 5 and 6

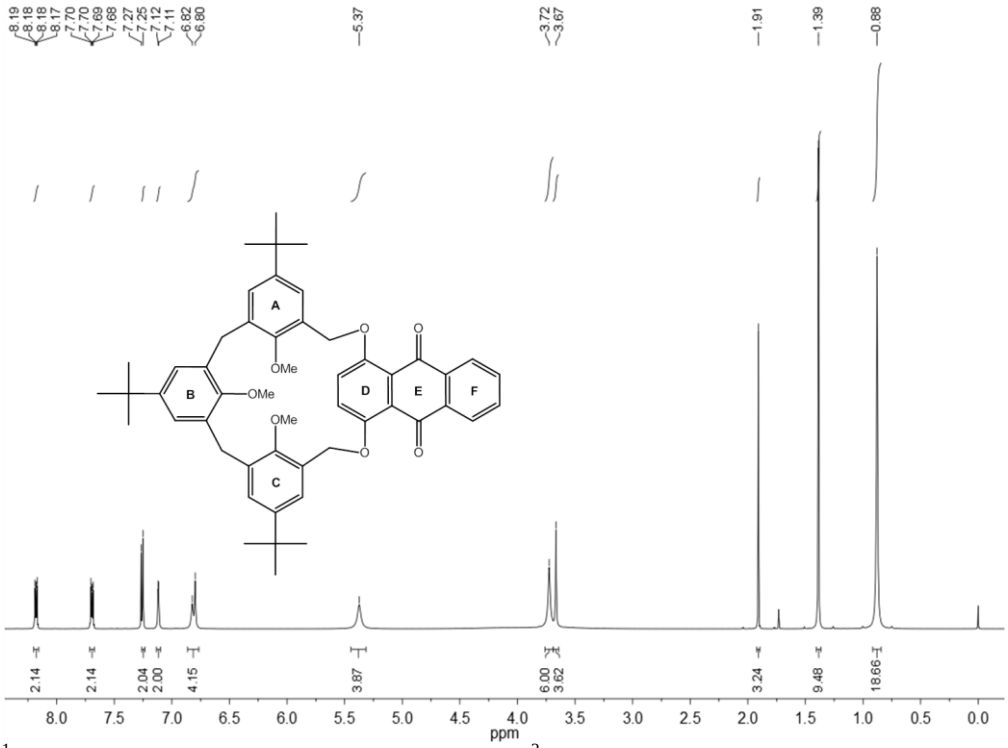



**Figure S4.** $^{1}$H-NMR spectra of compound **1** ($CDCl_3$, 293 K).[2]

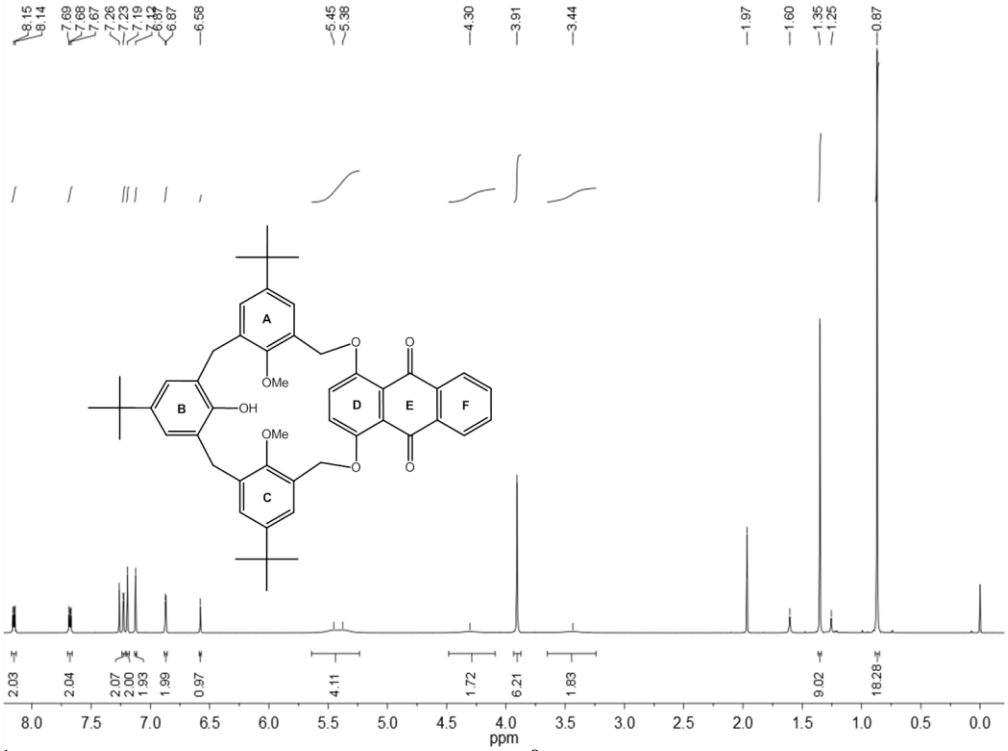



**Figure S5.** $^{1}$H-NMR spectra of compound **2** ($CDCl_3$, 293 K).[2]

[2] Solvent residual peaks: 1.25 ppm (grease), 1.60 ppm ($H_2O$), 7.26 ppm ($CHCl_3$); signals of adhesive and/or included acetonitrile at 1.97 ppm ($^{1}$H-NMR) and 1.7 ppm, 116.3 ppm ($^{13}$C-NMR).

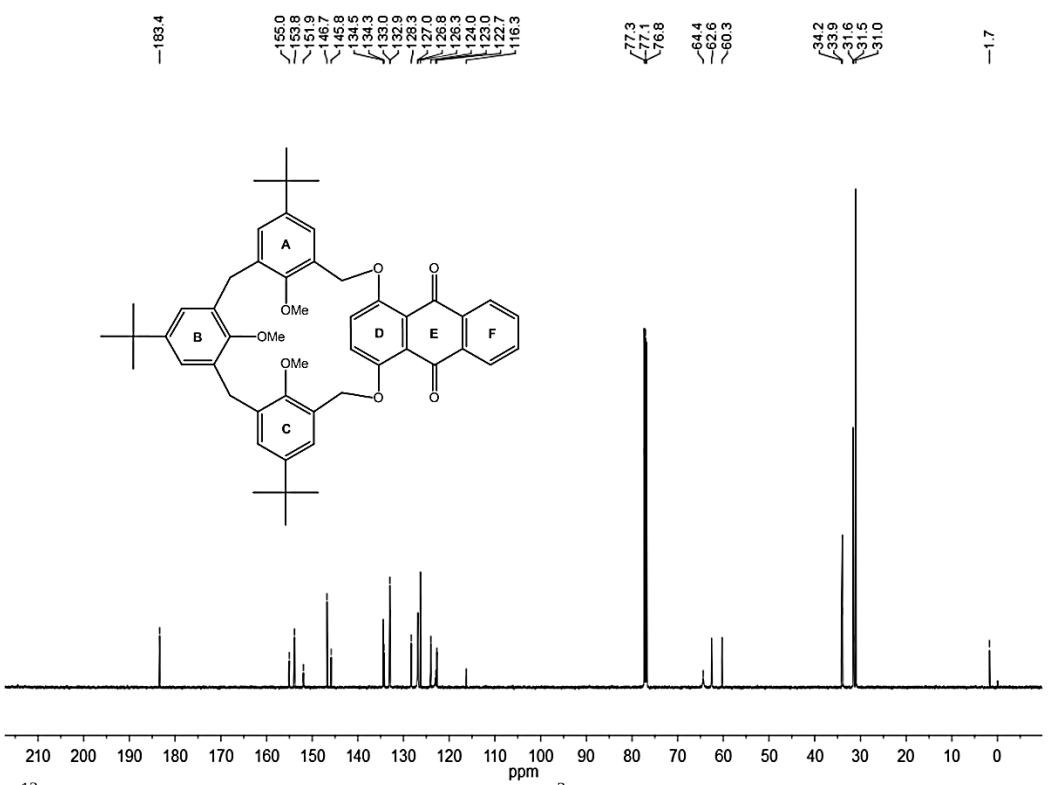



**Figure S6.** $^{13}$C-NMR spectra of compound **1** ($CDCl_3$, 293 K).[2]

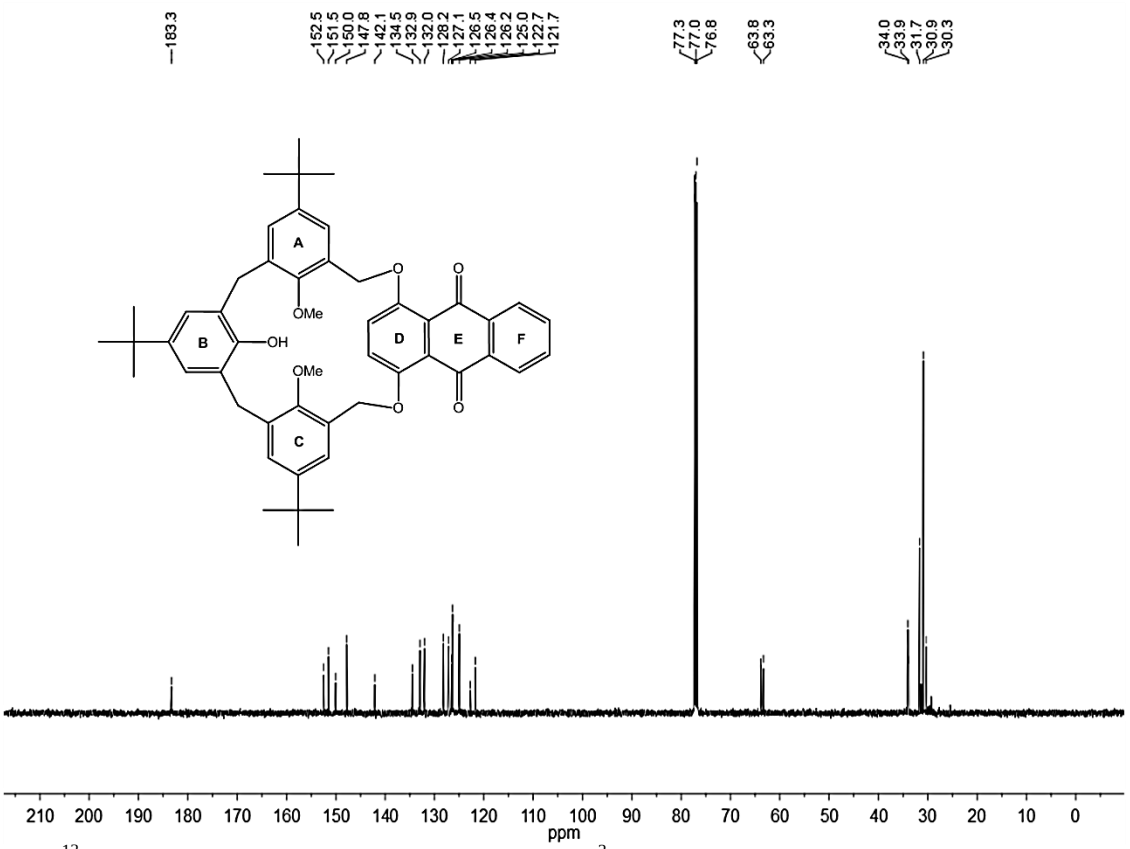



**Figure S7.** $^{13}$C-NMR spectra of compound **2** ($CDCl_3$, 293 K).[2]

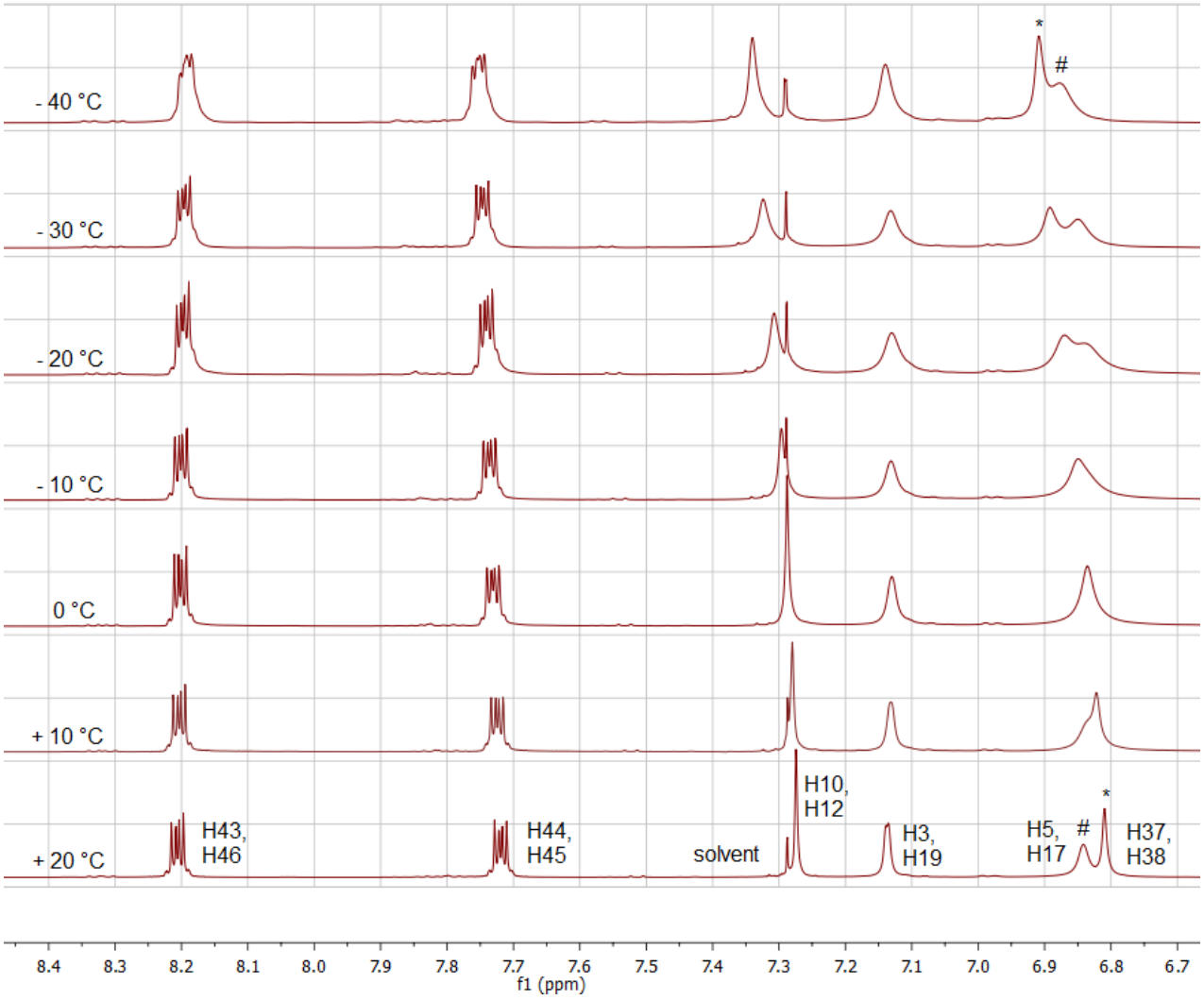



**Figure S8.** Detail of the $^{1}$H NMR spectrum of **1**at different temperatures in $CDCl_3$.

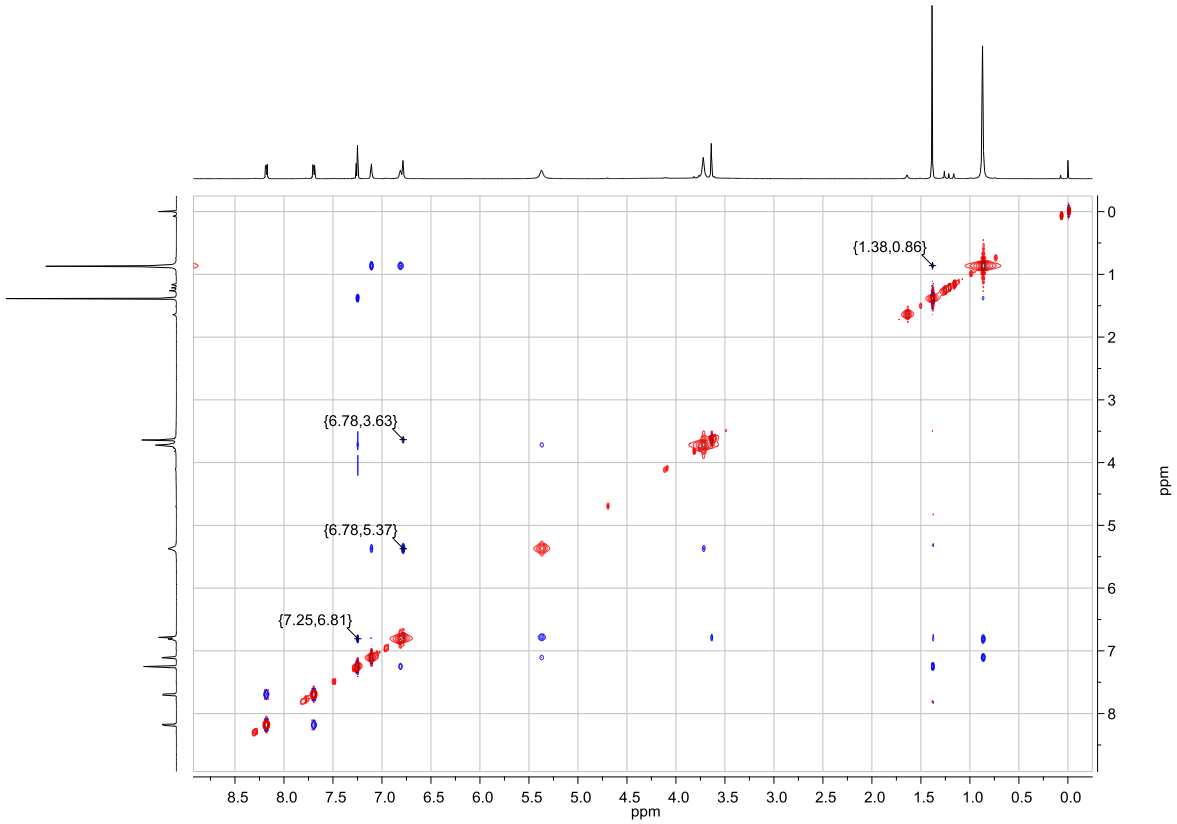



**Figure S9.** NOESY spectrum of **1** in $CDCl_3$ at 293 K.

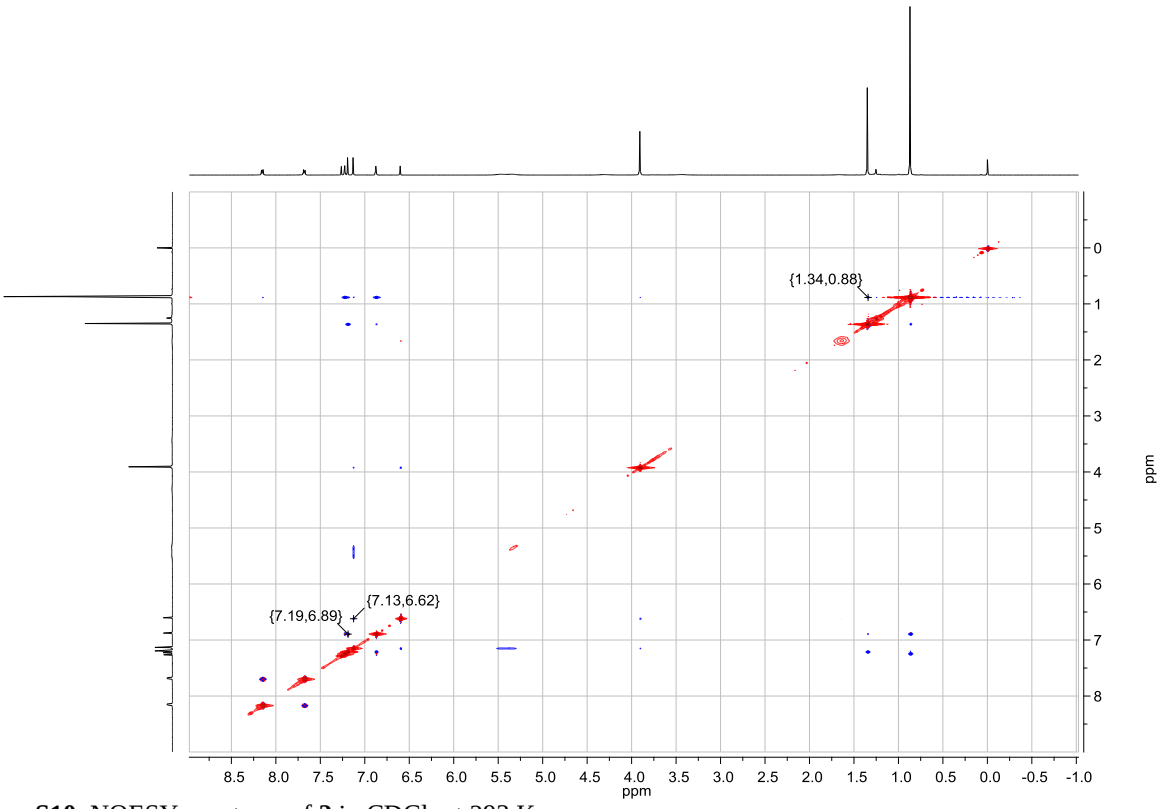



**Figure S10.** NOESY spectrum of **2** in $CDCl_3$ at 293 K.

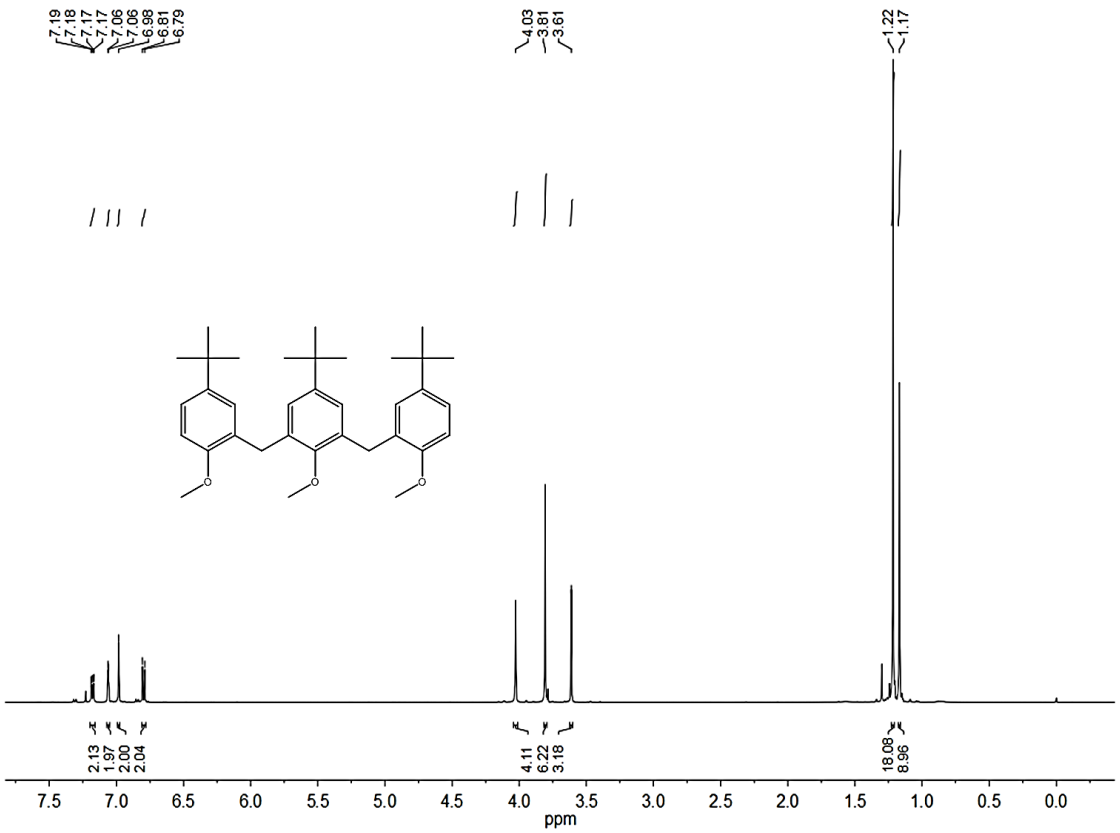



**Figure S11.** $^{1}$H-NMR spectra of compound **4** ($CDCl_3$, 293 K).

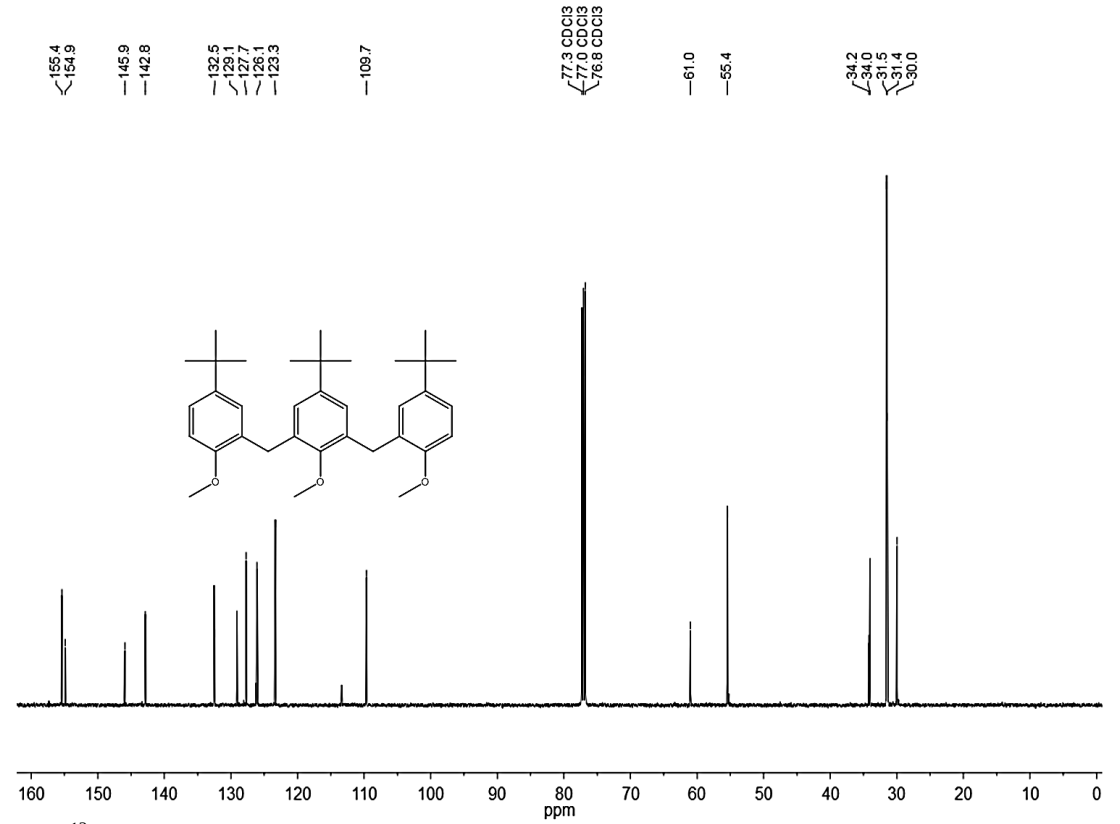



**Figure S12.** $^{13}$C-NMR spectra of compound **4** ($CDCl_3$, 293 K).

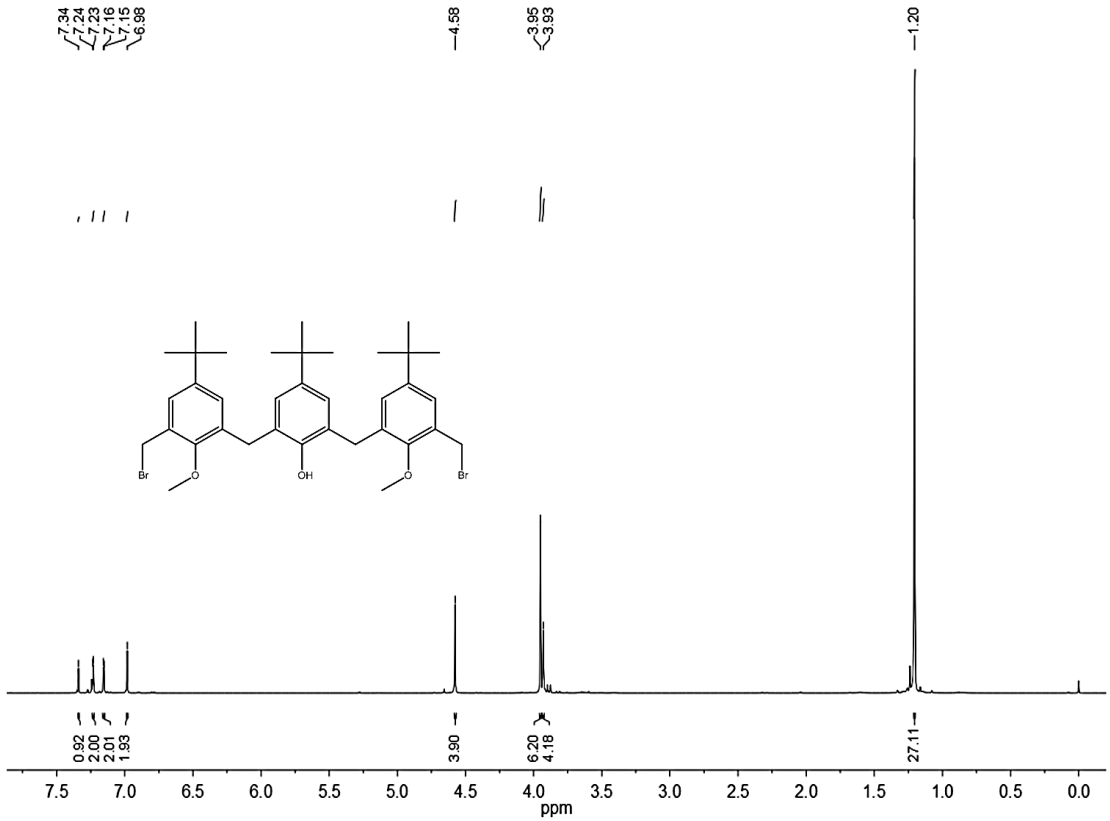



**Figure S13.** $^{1}$H-NMR spectra of compound **5** ($CDCl_3$, 293 K).

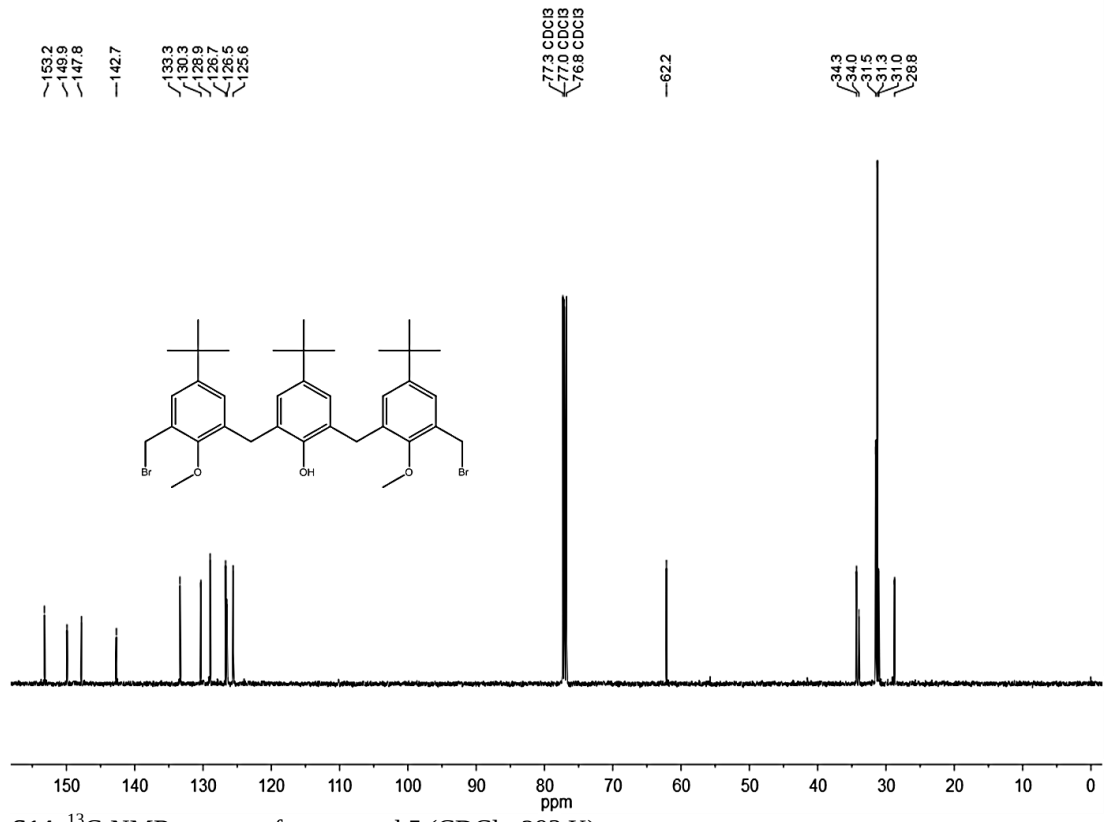



**Figure S14.** $^{13}$C-NMR spectra of compound **5** ($CDCl_3$, 293 K).

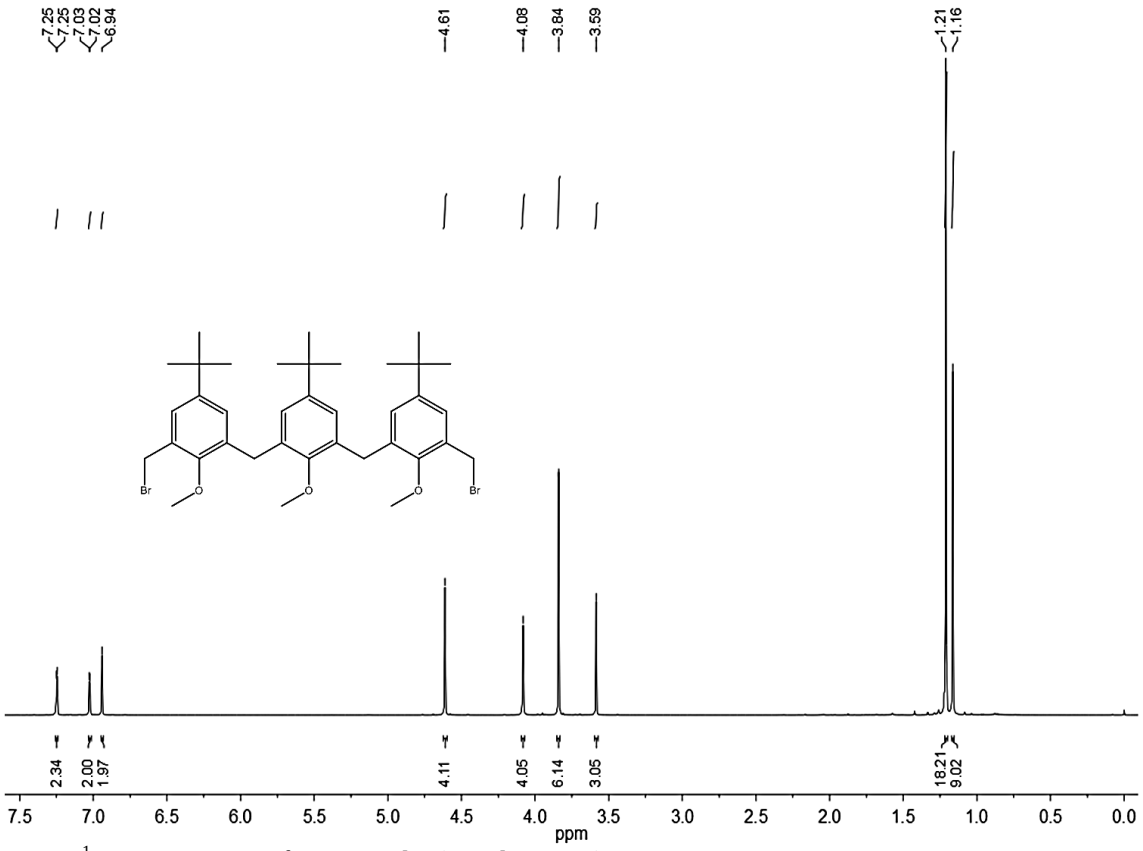



**Figure S15.** $^{1}$H-NMR spectra of compound **6** ($CDCl_3$, 293 K).

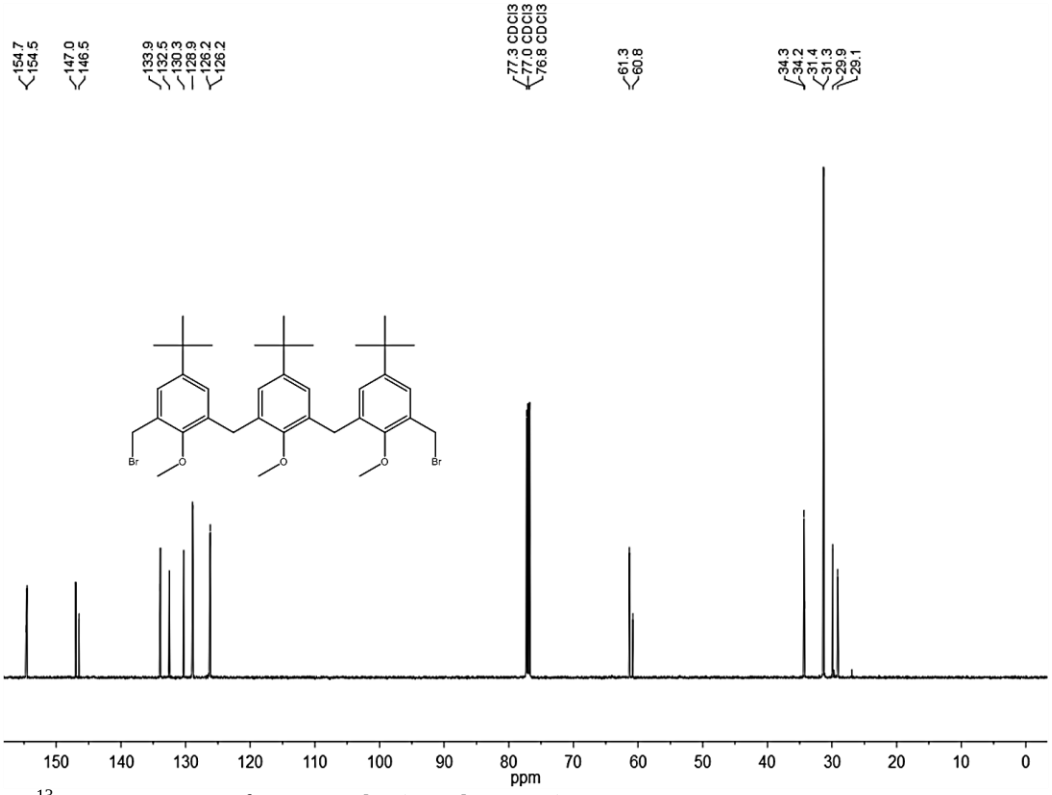



**Figure S16.** $^{13}$C-NMR spectra of compound **6** ($CDCl_3$, 293 K).